Labwide LDRD - Final Report

E. Y. Lau

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Lab-wide LDRD Final Report

Title: Experimental and Ab Initio Theoretical Search for Lanthanide Covalency for Enhanced Rare Earth Separations
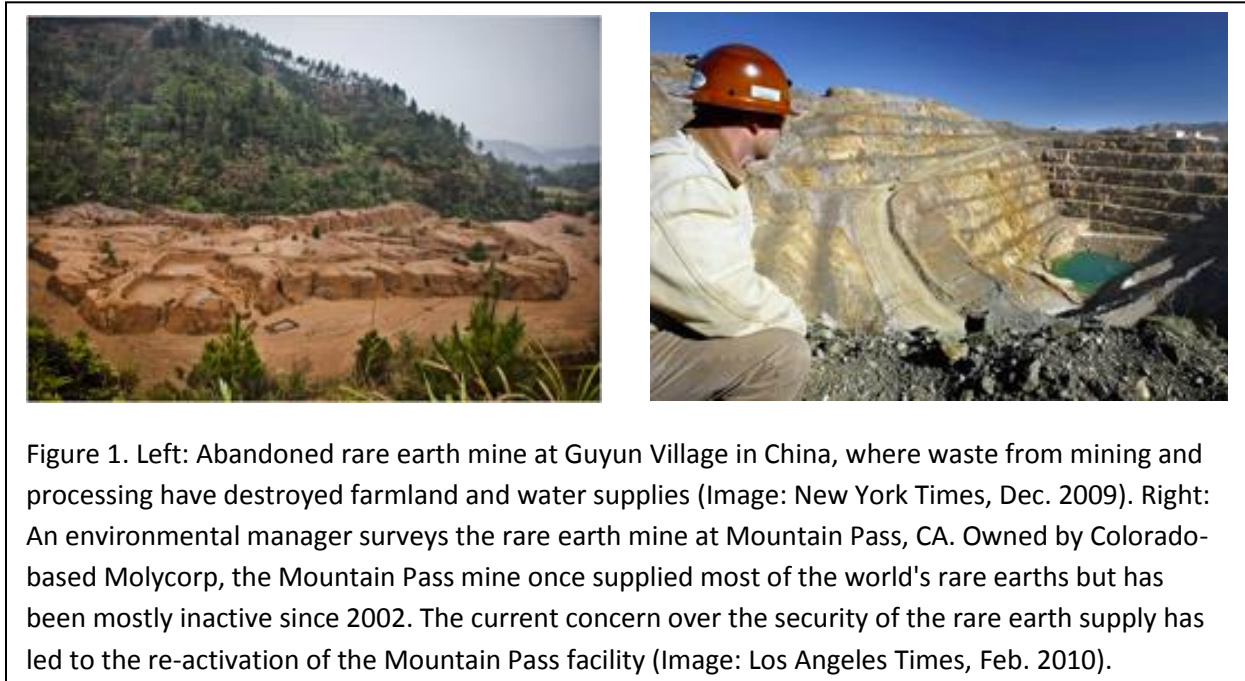
Lead principal investigator: Edmond Lau

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Project description
The objective of this project is to develop new concepts in lanthanide bonding that will ultimately lead to novel ligands for the efficient separation of rare earth elements. Specifically, we are searching for and characterizing covalent bonding interactions between lanthanides and main group elements. The project is a combined experimental and theoretical effort where targets complexes are proposed and synthesized in the laboratory, and theoretical calculations are carried out to gain insight into the nature of bonding in the synthesized complexes.

INTRODUCTION:

The rare earth elements (REE) refer to the lanthanide (Ln) elements with atomic numbers 57 to 71, plus scandium and yttrium. These materials are critical for some of the most important technological applications of today: electronic displays, high-efficiency lighting, and high-performance magnets for hybrid vehicles, wind turbines, and hard drives, to name a few. As demand is certain to increase, there is a growing concern over the availability of rare earths to meet future needs [US-DOE, 2011]. The main problem with ensuring a secure supply is that the

Figure 1. Left: Abandoned rare earth mine at Guyun Village in China, where waste from mining and processing have destroyed farmland and water supplies (Image: New York Times, Dec. 2009). Right: An environmental manager surveys the rare earth mine at Mountain Pass, CA. Owned by Colorado-based Molycorp, the Mountain Pass mine once supplied most of the world's rare earths but has been mostly inactive since 2002. The current concern over the security of the rare earth supply has led to the re-activation of the Mountain Pass facility (Image: Los Angeles Times, Feb. 2010).

process of mining and refining REE is environmentally damaging, generating large volumes of contaminated liquid waste. The U.S. was the global leader in rare earth production until the mid-1980's; U.S. production eventually declined due to the high cost of mitigating the associated environmental impacts. Today, China produces at least 95% of REE globally. However, this dominance has come at a severe environmental price, and the proliferation of illegal mining and processing activities remain a serious problem in China (Figure 1, left). Despite the

environmental concerns, the need to ensure a secure supply of REE has driven the U.S. to restart domestic production (Figure 1, right). The rare earths are actually not so rare; instead, they are widely dispersed and typically occur together in low-concentration ores. Much of the waste generated in REE production is due to the separation of the ores via solvent extraction [Nash, 1993]. In short, this is a method to separate compounds based on differences in solubility between two immiscible phases (typically an aqueous and organic liquid). A key step in this process is the use of an organic ligand (extractant) that selectively binds to the target species and maximizes the partitioning between the two phases. But because the rare earths are chemically very similar [Bünzli, 2006], currently available extractants have poor selectivity and hence separation is inefficient. There is a pressing need to develop new ways to efficiently separate rare earths in order to minimize the waste products, and consequently, the environmental impact of REE production. This development will require advances in our fundamental understanding of rare earth chemistry. Compared to the d-block transition metal elements, our understanding of the basic chemistry of the rare earths is not nearly as advanced and has largely been neglected within the U.S. research community [Adachi, 2010]. However, this trend is changing given the recent recognition of the critical role that REE plays in numerous essential technologies. Thus, our goal is to establish a position at the forefront of this important growth area by developing new concepts in lanthanide bonding that will ultimately lead to novel ligands for efficient separations.

The lanthanides (Ln) are f-block elements with partially filled 4f orbitals; the electronic configuration of the neutral gas-phase atoms is $[Xe]4f^n5d^{1-6}s^2$. In molecules and condensed phases, the ions typically assume a +3 oxidation state (Ln^{3+}) with electronic configuration $[Xe]4f^n$. It is generally accepted that the lanthanide 4f electrons are localized and atomic-like, and

do not participate directly in bonding. This is evidenced by the fact that transitions between the 4f states of Ln ions in condensed phases are sharp, narrow lines, indicating little interaction with the environment. These trends have led to the conventional view that Ln bonding is ionic, i.e., dominated by classical electrostatic forces (Coulomb and polarization) whose strengths are very similar across the lanthanide series. Currently, the rational design of ligands for intra-lanthanide separations largely relies on differences in the ionic radii of Ln^{3+} ions; these differences are especially subtle between adjacent elements on the periodic table. To improve the selectivity of ligands for lanthanide separations, we need to discover and exploit new types of bonding interactions. We hypothesize that the unoccupied 5d in Ln^{3+} ions can hybridize with donor ligand orbitals, thus contributing an appreciable degree of covalent character to lanthanide bonding (covalency is defined here in the general sense as either a partial or complete sharing of electrons between two atoms). The occupied 4f differ qualitatively in occupation number and symmetry even between adjacent elements in the periodic table, and thus the different 4f–5d interactions are expected to produce exploitable differences within the lanthanide group. This hypothesis is motivated by the following observations: 1) transitions between Ln 4f and 5d states are broad and sensitive to the environment, indicating that the 5d orbitals can interact with their surroundings [Bünzli, 2006]. 2) In rare earth intermetallic solids (high performance magnets fall under this category, e.g., $Nd_2Fe_{14}B$ and Sm_2Co_{17}), covalency between empty Ln 5d and occupied transition metal 3d is well established, and influences magnetic properties [Richter, 1998]. Molecular analogs of rare earth intermetallic complexes have been synthesized and characterized, and electronic structure calculations confirm the covalent character of the lanthanide transition metal bond [Butovskii, 2010]. 3) Ln complexes with σ-donating metalloids have also been shown to possess covalent character [Krinsky, 2011]. While the above examples

of lanthanide covalency are fundamentally interesting, they are not compatible with industrial solvent extraction processes. For such applications, we need ligands that are main group elements like carbon, nitrogen, and oxygen; the strongest interactions derive from the formation of multiple covalent bonds, i.e., both σ- and π-bonds. Multiple metal-ligand bonds with carbene (M=CHR), imido (M=NR), and oxo (M=O) ligands (R = alkyl or aryl group) are well-known for the transition metals and actinides; to date, there is a paucity of analogous examples for lanthanides. Nevertheless, ab initio electronic structure calculations on model Ce complexes containing $Ce(CH)_2$, $Ce(NH)$, and CeO fragments find σ- and π-interactions between Ce and C, N, O [Clark, 2005]. Experimentally, Ln-imido (Ln=NR) complexes have been studied the most; all the isolated Ln-imido complexes contain an imido fragment bridging two Ln metal centers [Trifonov, 1991; Emelyanova, 1994; Xie, 1999; Wang, 1999; Chan, 2002; Beetstra, 2003]. An example of the first Ln-phosphinidene (Ln=PR) complex has also been reported. Thus, the available body of evidence suggests that lanthanide covalent bonding with main group elements is possible, providing a new property to target in the development of selective ligands for lanthanide intra-group separations.

METHOD:

Computation:

All calculations were performed using the program Gaussian09. The recent density functional TPPSh was used for these calculations [Tao, 2003]. This functional has been shown to adequately reproduce the geometries of lanthanide complexes. All calculations of the lanthanide metals ions utilized the small core Stuttgart/Dresden empirical core potential (ECP)

[Cao, 2002] and the cc-pVDZ basis set was used for all other atoms [Dunning, 1989] except Te which used the cc-pVDZ-PP ECP [Peterson, 2003]. All the lanthanides were assumed to be in the +3 oxidation state and in their high spin state. All calculations were converged to the default values. Harmonic frequency calculations were performed on all the structures to ensure the geometry was a minimum.

Synthesis:

Our laboratory uses Schiff base ligands due to synthetic ease and ability to manipulate their steric and electronic properties of the ligand. We will synthesize three different ligands that chelate Ln in three positions. These ligands can be used to create a ligand platform that will foster stable, isolable lanthanide compounds. The synthesis should be straightforward from the lanthanide trichlorides, $LnCl_3(THF)_4$, (Ln = Ce, Gd, Lu; THF = tetrahydrofuran, a common organic solvent) with two equivalents of the sodium salt of our ligand of choice. Ln-ligand multiple bonds show the most significant interaction thus our first targets will be Ln-imido complexes that contain a formal Ln-nitrogen double bond. Reactions with the magnesium imido (Mg=NPh) reagent to yield Ln-imido complexes will be attempted starting with $LnCl_3(THF)_4$. Almost certainly, the reaction of $LnCl_3(THF)_4$ with Mg=NPh will yield a polymetallic cluster but a dimer containing a bridging imido ligand would be predicted to form with reaction of two equivalents of compound 1 with Mg=NPh. We will then react the monochloride species with KEAr (E = S, Se, Te; Ar = aryl group) in order to exchange the chloride for EAr to produce Ln-chalcogenolate complexes. Finally, reactivity with one equivalent of $LiPPh_2$ will be attempted to produce Ln-phosphinidene (Ln=PR) compounds in order to study a rare example of a lanthanide-

phosphide bond. Characterization will be done using ^{1}H and ^{13}C NMR spectroscopy, as well as other NMR active nuclei that may be possible such as ^{15}N, ^{31}P, and [77]Se. Ultraviolet-visible-near infrared (UV-Vis-NIR) and EPR spectroscopies will be used to study the electronic structure of the compounds while X-ray crystallography will definitively determine the molecular structure.

RESULTS:

To study the possibility of *f*-block bonding, we chose two different ligands to that utilize the same atoms (sulfur and selenium) to coordinate the lanthanides. A previous studied ligand (imidodiphosphinochalcogenide [N(EPPh$_2$)$_2$]$^-$, where E = O, S, Se, or Te) binding some of the lighter lanthanides (La, Ce, Pr, Pm, and Eu) was used as a reference [Ingram, 2008]. We extended the study of this ligand to all the lanthanides and lutetium. To simplify the calculations, the two phenyl groups were replaced with hydrogens. All the coordinating
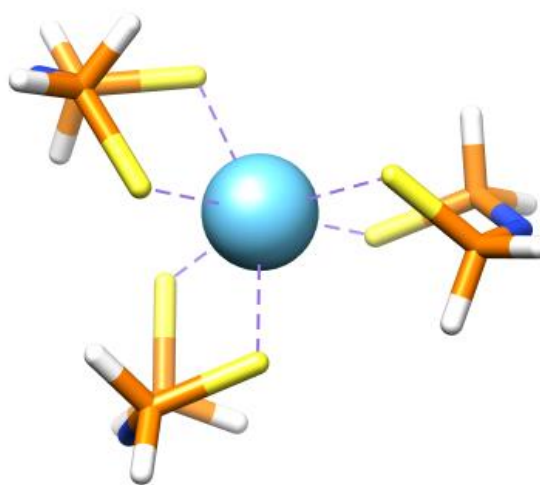

Figure 2. Optimized structure of La[N(SPH)$_2$)$_2$]$_3$.
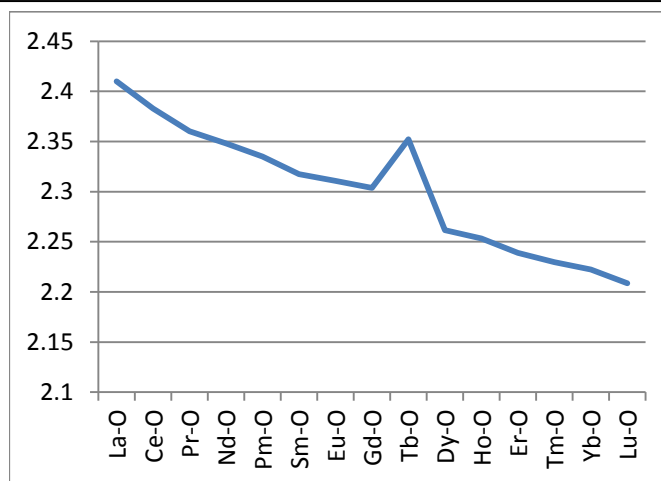

Figure 3. Average bond length (angstroms) of lanthanide-oxygen for Ln[N(OPH2)2]3 structures.

geometries for these ligands binding any lanthanide were octahedral (Figure 2). All geometries

were converged to default cutoffs except Ho[N(TePH$_2$)$_2$]$_3$. Three of the convergence cutoffs were met but the maximum displacement could only converged to 0.002558 au Å^{-1}.

The bond length between the lanthanide and hard donor oxygen atoms of the imidodiphosphino-chalcogenide ligand shows a steady decrease with increasing atomic number, except for terbium (Figure 3). Additionally, there is very little variation in the bond lengths for the individual ligands to the lanthanide.
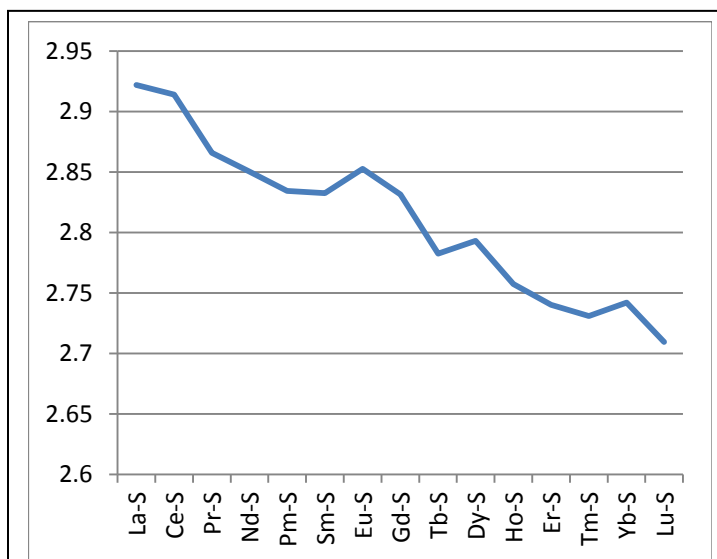
Figure 4. Average bond lengths (angstroms) for lanthanide-sulfur of Ln[N(SPH$_2$)$_2$]$_3$ structures.

The variation tends to be less than 0.01 Å for almost all the imidodiphosphinochalcogenide ligands studied. The bond lengths between the lanthanides and the soft donor sulfur and selenium show a similar trend (Figure 4 and 5). The bond lengths reduce as the atomic number increase for the lanthanides but it is not steady. Additionally, there
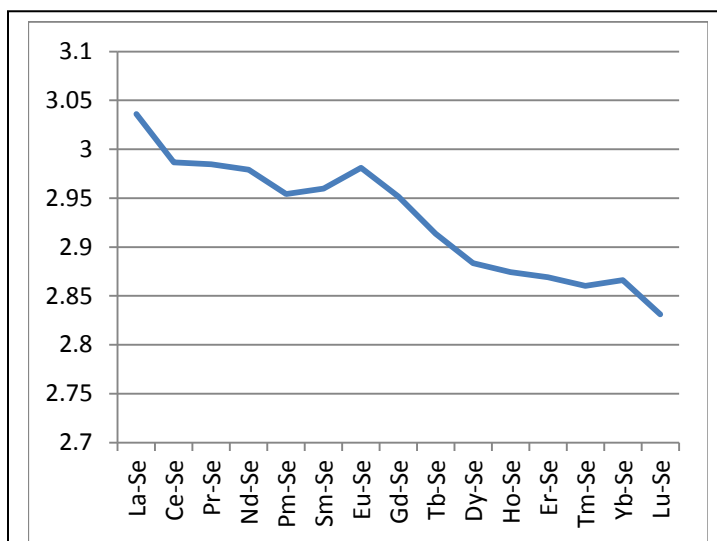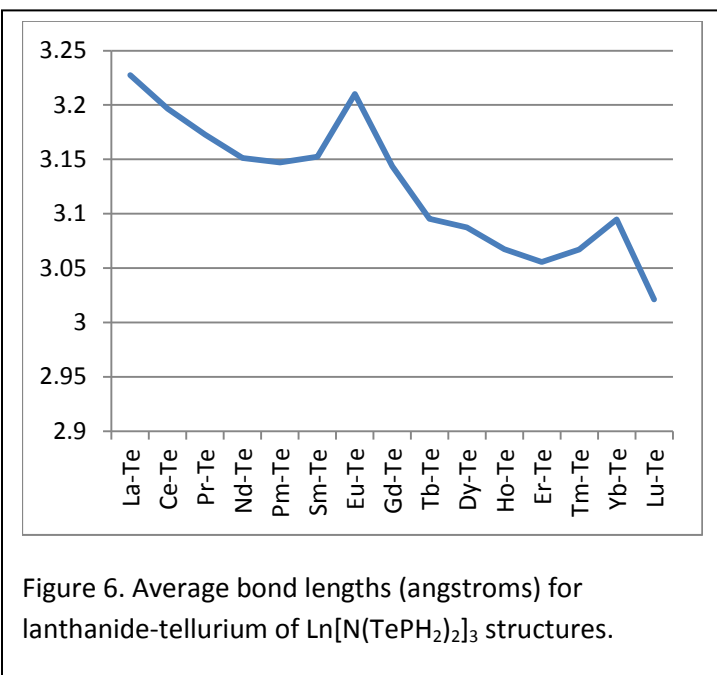
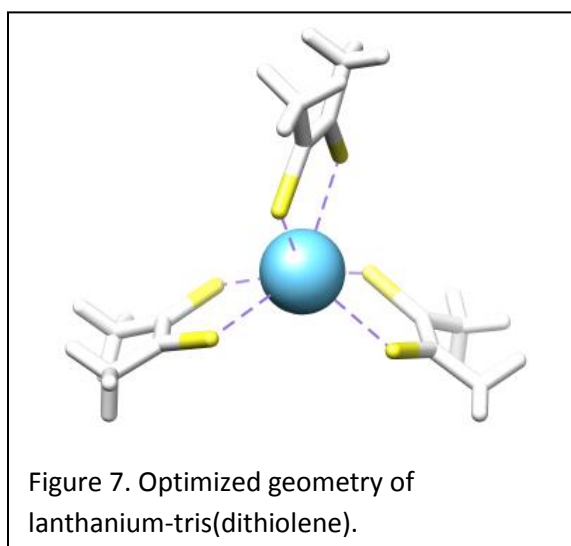Figure 5. Average bond lengths (angstroms) for lanthanide-selenium of Ln[N(SePH$_2$)$_2$]$_3$ structures.

is a jump in bond length at europium for both ligands. The bond lengths for the lanthanide-tellurium have a similar trend to the soft donors sulfur and selenium but unlike these atoms there

is some asymmetry in the bond lengths for thulium and ytterbium (Figure 6). In the case of the thulium, one of the ligands was bound more weakly (average Tm-Te distance 3.057 Å) than the other two ligands (average Tm-Te distance 3.067 Å). In the case of ytterbium, the ligands trans to each other have an effect of the bond length likely due to Jahn-Teller splitting.

We can compare the above bond lengths with those calculated for dithiolene and diselenene ligands that are efficient at stabilizing metals with high oxidation states [Meskaldij, 2010]. The geometry adopted by these ligands differs from the octahedral imidodiphosphino-chalcogenide ligands. The tris-complexes of both dithiolene and diselenene have a trigonal prismatic geometry (Figure 7) when bound to lanthanides although the coordination geometry tends to resemble octahedral as the lanthanide atomic number increases. In addition to the change in geometry, the bond lengths for these ligands can have large variations. In the case of lanthanum-dithiolene, the lanthanum-sulfur bond lengths vary from 2.88 to 2.95 Å. This is even more pronounced for lanthanum-diselenene which have bond variations from 2.90 to 3.04 Å.

Figure 6. Average bond lengths (angstroms) for lanthanide-tellurium of $Ln[N(TePH_2)_2]_3$ structures.

Figure 7. Optimized geometry of lanthanium-tris(dithiolene).

Table 1. Lanthanide-sulfur distances (angstroms) for lanthanide-tris(dithiolene) complexes.

La-S	2.91	2.9518	2.8844	2.9228	2.8992	2.9375
Ce-S	2.8831	2.9121	2.8605	2.8868	2.8744	2.9029
Pr-S	2.8678	2.8856	2.8494	2.8633	2.8405	2.89
Nd-S	2.8528	2.8528	2.8387	2.8387	2.8529	2.8386
Pm-S	2.8385	2.8501	2.8357	2.8316	2.8231	2.8531
Sm-S	2.8531	2.8735	2.8431	2.8647	2.852	2.8658
Eu-S	2.8825	2.8825	2.8802	2.8802	2.8827	2.8801
Gd-S	2.8254	2.8253	2.8253	2.8254	2.8254	2.8254
Tb-S	2.753	2.7706	2.7984	2.7954	2.7229	2.6907
Dy-S	2.7907	2.7907	2.7537	2.7537	2.791	2.7536
Ho-S	2.7515	2.7514	2.7437	2.7439	2.7515	2.7438
Er-S	2.733	2.7334	2.7326	2.7382	2.7388	2.7334
Tm-S	2.7249	2.7363	2.7193	2.7382	2.7205	2.7297
Yb-S	2.7256	2.7257	2.7256	2.7257	2.7257	2.7256
Lu-S	2.6933	2.6933	2.6933	2.6932	2.6931	2.6934

We have performed population analyses on the lanthanides to investigate the variation in electron density. Although there are drawbacks to population analysis, it can be an useful tool to compare variations in electronic structure. Atomic polar tensor (APT) charges were used for this comparison. The APT charges on the
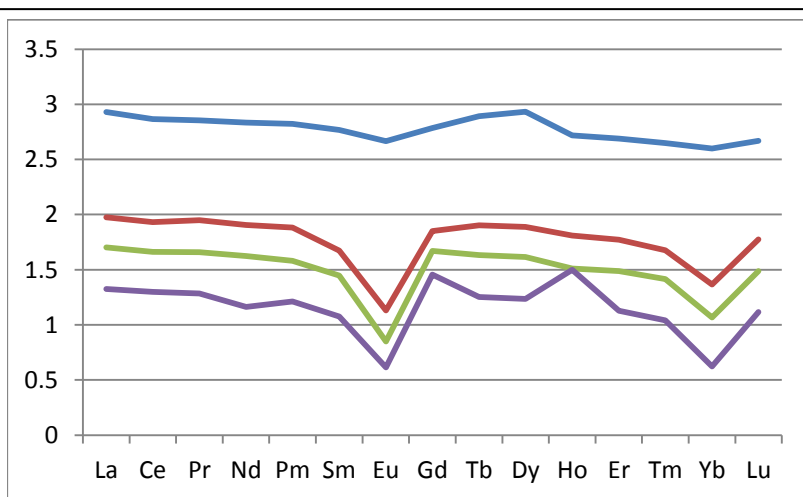

Figure 8. APT charges on the lanthanides by coordinating atoms (oxygen (blue), sulfur (red), selenium (green), and tellurium (violet).

lanthanide metal for any of the Ln[N(OPH$_2$)$_2$]$_3$ complexes was close to the expected +3 charge (Figure 8). Interestingly, when the coordinating atom is sulfur the lanthanide metal gains electron density (almost one electron). This trend increases from selenium to tellurium. Interestingly, the dithiolene and diselenene appear to share more electron density with the lanthanides than the

imidodiphosphinochalcogenide ligands (Figure 9). Additionally, lanthanides with approximately half-filled orbitals receive the most electron density from the dithiolene and diselenene.

To further quantify the increased electron density on the lanthanides by the dithiolene and diselenene, Mulliken spin densities were calculated for the complexes. For the $Ln[N(OPH_2)_2]_3$ metal ions, the spin densities on the lanthanides are very close to
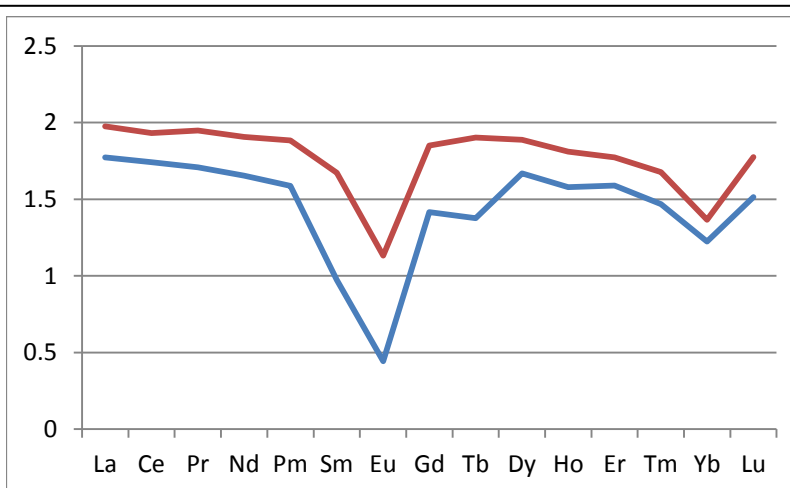

Figure 9. Comparison of APT charges for lanthanides coordinated by $[N(SPH_2)_2]_3$ (red) and tris-dithiolene (blue).

the expected integer values. The softer donors (S, Se, and Te) show enhanced electron spin density for the lighter lanthanides until gadolinium which has reduced electron spin density. Interestingly, there is little variation in the spin density for the lanthanides when coordinated by imidodiphosphinochalcogenide ligands consisting of sulfur, selenium, or tellurium. For the dithiolene and diselenene ligands, there is enhanced electron spin density for the lanthanides. Unlike the imidodiphosphinochalcogenide ligands, the electron spin density of gadolinium has increased by one electron. Additionally, terbium-diselenene has almost 2 electrons more than the expected value.

We endeavored to synthesize ligands that have been previously reported that were sterically crowded enough to support only monometallic lanthanide complexes so that metal-ligand multiple bonds may be possible. Those attempted are shown in Figure 10. Ligand A, iminophenolate

Table 2. Mulliken spin density of lanthanide coordinated to imidodiphosphinochalcogenide ligands.

	O	S	Se	Te
La	0	0	0	0
Ce	1.02809	1.043483	1.051821	1.06565
Pr	2.033655	2.083414	2.101192	2.13312
Nd	3.03446	3.122527	3.124426	3.165101
Pm	4.044988	4.152231	4.203462	4.271411
Sm	5.08479	5.300953	5.349015	5.454683
Eu	6.115532	6.5056	6.589074	6.745235
Gd	7.186592	6.736109	6.745658	6.760533
Tb	6.016829	6.072598	6.101936	6.154296
Dy	5.064682	4.984843	4.994729	5.00616
Ho	3.991491	4.021592	4.042998	4.062598
Er	2.985504	2.988683	2.991355	2.989926
Tm	1.961622	1.900861	1.895524	1.852496
Yb	0.954348	0.765894	0.721757	0.624254
Lu	0	0	0	0

and B, benzenedithiol, are redox-active so we thought we may be able to take advantage of those electronic properties. The monoanionic ligand C, β-diketiminate (or NacNac), is a sterically encumbering ligand. Unfortunately, lanthanide salts are very insoluble so we were not able to isolate the lanthanide complexes to conduct further reactivity. Our synthetic group was able to publish two papers that acknowledge LLNL-LDRD funding: Chem. Eur. J. 2013, 19, 16176 [1] and Nat. Chem. 2014, 6, 919 [2]. Both of these papers were collaborative efforts with

Table 3. Mulliken spin density of lanthanide coordinated to dithiolene and diselenene ligands.

	S	Se
La	0.097095	0.088015
Ce	1.14988	1.147983
Pr	2.210863	2.218367
Nd	3.252418	3.249364
Pm	4.329537	4.339875
Sm	5.562476	5.563032
Eu	6.78012	6.882383
Gd	7.622037	7.656932
Tb	6.301934	7.783318
Dy	5.098111	5.09524
Ho	4.143543	4.15461
Er	3.121432	3.108809
Tm	2.035825	1.998231
Yb	0.895109	0.817858
Lu	0.12349	0.100174

another synthetic group which makes U=N metal-ligand multiple bonds as well as U-E, E = S, Se, bonds, both of which were components of the original proposal.

CONCLUSIONS:

Although we were not successful in synthesizing novel ligands for coordinating lathanides, ab initio calculations were useful in showing that ligands based on dithiolene and diselenene could have the desired property of having the ability to covalent bonding to some lanthanides.
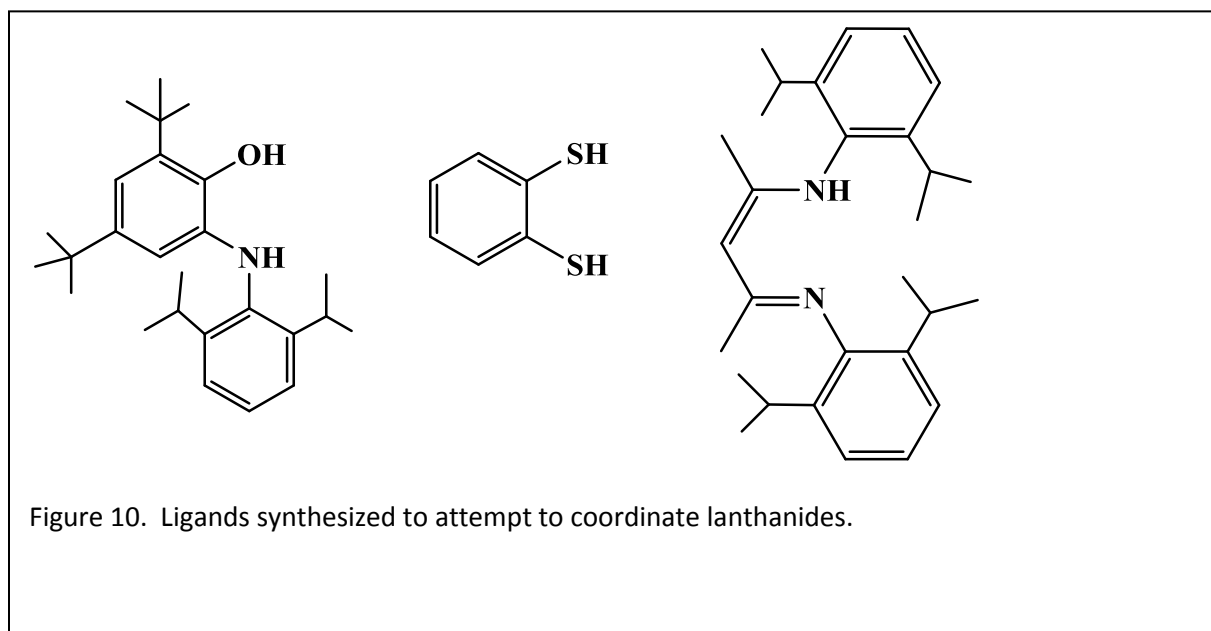

Figure 10. Ligands synthesized to attempt to coordinate lanthanides.

ACKNOWLEDGEMENTS:

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